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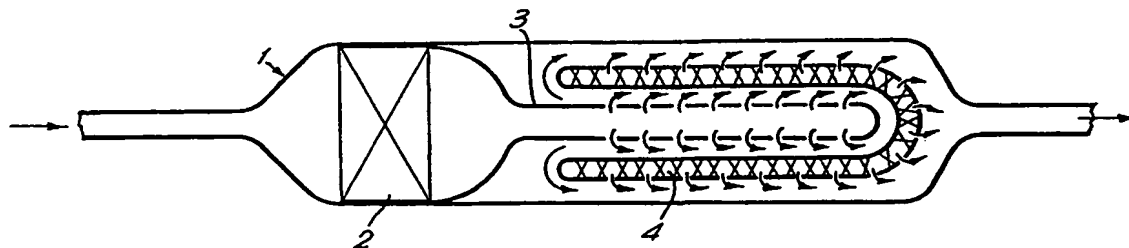
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(57) Abstract

A cost-effective solution to removing particulates from diesel, especially light-duty diesel engines incorporates an oxidation catalyst (2) effective to convert NO in the exhaust from the engine to NO₂ and a particulate trap (4) which traps no more than 85 % by weight of the particulate, optionally by permitting gas to by-pass the trap.

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IMPROVEMENTS IN EMISSIONS CONTROL

The present invention concerns improvements in emission control, and more especially it concerns the control of emissions from diesel engines.

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↓ Diesel engines fall into two main categories, namely heavy duty, being principally large engines for trucks, buses and prime mover vehicle engines, ships and boats and stationary engines, and light duty engines, used in smaller trucks and cars. With the increasingly demanding regulation of emissions from all sorts of engines, attention is now being paid to control of emissions such as particulates and NO_x from diesel engines. We have, in EP 341,832, described a device marketed as the Continuously Regenerating Trap ("CRTTM") by Johnson Matthey. This device traps sooty particulates and causes their combustion by exposing them to NO₂ generally generated by catalytically oxidising NO present in the exhaust stream. This device has met with considerable success in controlling particulate emissions from heavy duty diesel engines, and can achieve zero emissions of particulate. That is, the CRT as marketed is approximately 100% effective to remove particulates (as defined in the regulations).

We have realised that a conventional CRT may not be cost-effective to control emissions to European Stage III, IV, or higher, regulations from light duty engines. A number of different options for controlling particulates and NO_x are available, and engine manufacturers have hitherto favoured engine design and management solutions. In general, engine design itself can satisfy European Stage II emissions standards as regards NO_x and particulates, but the characteristics of the diesel engine are such that engine design cannot improve upon about 0.4g/Km particulates without a serious increase in NO_x, which is difficult to deal with under lean conditons. There still remains, therefore, a need for effective systems to meet these emission regulations whilst increasing engine design options.

The present invention provides an emission control system for diesel engines comprising a source of NO₂, especially an oxidation catalyst effective to convert a portion of NO in the exhaust gas from said diesel engine into NO₂, and a particulate trap characterised in that at most 85% by weight of total engine-out particulates are collected and

combusted in the presence of said NO_2 in said trap. According to various embodiments of the present invention, the quantity of particulates collected and combusted may be at most 85%, 60% or at most 50% by weight. It is, however, important that all particulates collected are combusted (over several operating cycles, but not necessarily over a single operating cycle), in order to avoid accumulation and blocking of the filter, causing build-up of back pressure with consequent degradation of engine performance.

Another embodiment of the present invention comprises an oxidation catalyst effective to convert a portion of NO in the exhaust gas into NO_2 , or other source of NO_2 , and particle trapping means which means permits a portion of the exhaust gases to escape the trapping means. Desirably, the trapping means is designed to be "fail-safe", that is whilst it is effective to capture 50wt% or more of sooty particulates under normal conditions, the trapping means decreases its collecting efficiency whether by exhaust by-passing the trapping means or otherwise, if the collecting means becomes "saturated" or clogged up. This concept is, we believe, new in diesel exhaust treatment systems.

The invention further provides a method for the control of at least sooty particulates from diesel engine exhausts by trapping and subsequently combusting said particulates by reaction with NO_2 , characterised in that at most 85wt% of the particulates are trapped for subsequent combustion.

The source of NO_2 is especially conveniently an oxidation catalyst of generally known type, capable of converting at least a portion of the NO contained in diesel exhaust gases into NO_2 . However, the present invention includes within its scope variations including other sources of NO_2 . Such sources could include compressed NO_2 , other chemical sources which decompose or react, possibly over a catalyst, to yield NO_2 , such as nitric acid, ammonia, urea, etc. The invention includes within its scope all ways of making NO_2 from the components of the exhaust gases. These may include: adding one or more catalytic components to the fuel, so that the components deposit on exhaust components including the filter; catalysing the filter or parts thereof with catalysts active at low

temperatures to convert NO to NO₂; utilising a plasma to generate NO₂ by treatment of all or a portion of the exhaust gases, and other methods available to the skilled person.

In the invention, the particulate trap, or trapping means, is designed to be less than 100% effective, and desirably this brings several advantages, the first of which is considerably reduced back pressure. Light duty diesels are very much less capable of coping with back pressure from exhaust gas systems than heavy duty diesels, because they tend to be of smaller capacity and power, and in extreme cases the engine can be ruined.

The present invention is also intended to cater for some of the problems that can arise in practical usage of light duty diesels. If such engines are used in small cars or vans which are used at low speeds in towns for large portions of their operations, the exhaust gas temperature tends to be quite low, perhaps not more than 100-120°C. Under these conditions, although sooty particulates are generated in less quantities than under heavy load, the temperature is below that for the most efficient oxidation of NO to NO₂ and hence there can be insufficient NO₂, or the reaction temperature is too low for effective combustion of the sooty particles. Accordingly, for many vehicles for much of the time, the trapping means should collect sufficient of the particles to meet the emission regulations, but using a design that collects such particulates for subsequent combustion when conditions are improved, and permits the exhaust gas to pass through without excessive back pressure. In such systems, at least 50wt% of particulate matter is trapped and subsequently combusted when operating conditions in the same or subsequent operating cycles are improved.

It will be recognised that the prime purpose of the invention is to remove a proportion only of the particulates from the exhaust gas stream. This is intended to be adequate to meet the appropriate emission regulation when combined with engine design and management improvements. The reduced efficiency in collection of particulates of the present invention brings about a significant reduction of cost, however, from a reduced volume and weight for both the catalyst and the trap compared to the state of the art CRT designed for such an engine.

The oxidation catalyst may be any that is effective to convert sufficient NO to NO₂, and is suitably a high platinum loading catalyst carried on a ceramic or metal honeycomb catalyst support. It is envisaged that in addition to reducing volume and weight of the catalyst, savings may be made in precious metal loading, thus reducing the cost yet further.

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The particulate trap may suitably be a woven or knitted wire mesh or perforated metal or a suitable ceramic material. Preferred traps include especially those known as wall flow filters. The trap is suitably designed for each individual engine design, because the particulate emissions differ significantly from engine to engine. The trap may, but need not, carry a catalytic coating intended to initiate combustion at lower temperatures.

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Continuing development of the inventive concept of the present invention has led to studies of flow and pressure patterns within such exhaust treatment systems. A further embodiment of the invention, in which the trap has peripheral bypass through which the exhaust gases flow only when the central portion of the trap becomes blocked, is particularly preferred. The flow of the gases can be directed to the central portion by a variety of means, including particularly baffle plates or cones, metal lips and the like, but we have found that extending the catalyst in the peripheral area is particularly simple and effective to reduce gas flow rates in that region.

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A preferred embodiment of the present invention combines the emission control system with NO_x control means. The NO_x control may be achieved in a number of ways including exhaust gas recirculation, using a NO_x conversion catalyst downstream of the trap or, more preferably, combining the trap system with a NO_x absorbent. Such NO_x absorbents are known to those skilled in the art and may utilise an alkaline earth metal oxide such as baria or calcia or other suitable materials. Together with the trap system of the present invention, such an absorbent can permit extremely useful control of emissions, for example up to about 80% removal of particulates combined with up to about 80% removal of NO_x. The NO_x trap is desirably a single through-flow canister, which may be regenerated by periodic enrichment of the exhaust gas in a number of ways. In an even more preferred embodiment, the trap system of the invention is combined with a lean-NO_x

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catalyst and a NOx trap. A particularly desirable embodiment is where the NOx trap is effective to trap the NOx at low temperatures and releases NOx at higher temperatures, *eg* about 250°C, at which temperatures NOx may more readily be converted and/or used in the particulate combustion of the present invention.

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When using the presently-preferred platinum-based catalyst, the present invention should be used with fuel of not more than 50ppm sulphur, and preferably below 50ppm sulphur, more preferably below 10ppm sulphur. Other catalyst systems may have a wider range of fuel sulphur levels.

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The invention may be better appreciated by reference to the accompanying drawings, in which:

Figure 1 is a schematic cross-section of a first embodiment of the invention,

Figure 2 is a schematic cross-section of a second embodiment of the invention, and

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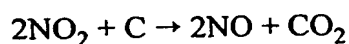
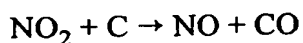
Figure 3 is a schematic cross-section of a further embodiment of the invention, and

Figure 4 is a schematic cross-section of a yet further embodiment.

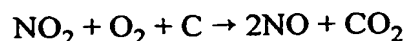
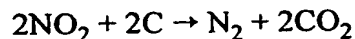
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Referring to Figure 1, a canister is to be mounted in the exhaust system of a light duty diesel, *eg* a 1.9 litre Tdi engine. The canister, 1, contains an oxidation catalyst, 2, which is a platinum catalyst carried on a 100cells/sq in metal honeycomb substrate. Particulate passes through the catalyst. A perforated gas distributor, 3, is mounted downstream of the catalyst, and surrounding the gas distributor is a sintered stainless steel filter, 4, which is located centrally within the canister. It can be seen that it is possible for the exhaust gases to by-pass the filter if the filter becomes clogged. Under ideal conditions, the filter collects sooty particles which are continuously combusted in the NO₂ generated by the catalyst, according to one or more of the equations:

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Under non-ideal conditions, that is at low exhaust gas temperatures, a portion only of the particulate is collected in the filter, and most of the exhaust gas by-passes the filter. Returning to higher exhaust gas temperatures permits the combustion reaction to re-start and the particulate can be totally removed from the filter.

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Referring to Figure 2, an embodiment is shown which permits substantial accumulation of particulate without by-pass, but using a filter, 5, which is not 100% effective. The same items as in Figure 1 are identified using the identical reference numerals. There is sufficient capacity to accumulate particulate under all normal operating conditions.

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Figure 3 utilises a slightly different by-pass design to that of the embodiment of Figure 1. The particulate is collected by impingement on a baffle plate, 6, and is shown by mass, 7. The baffle plate may itself be porous to gas or act as a filter. As exhaust gas temperatures rise, the hot gases immediately contact the collected particulate and quickly cause combustion. This design may comprise electrical heating of the collection area on plate 6, creating a hot spot to initiate combustion. In a further design variation the baffle plate may comprise upstanding walls, giving a U-shaped cross-section.

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A preferred embodiment is illustrated in Figure 4. Engine exhaust gas passes through catalyst 2, which is provided with a peripheral lip 2a. The resulting increased resistance to flow in the peripheral region causes the majority of the gases to flow through the central, filtering, region of trap 4, (4a) rather than through the open peripheral bypass region (4b). Thus under normal operating conditions, negligible quantities of the exhaust gases bypass the filter, but if the filter becomes blocked with particulate, the system is fail-safe and the gases bypass the filter. Surprisingly low back pressures result from this system.

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The above Figure 4 embodiment was tested fitted to a commercially available 1.9 litre Tdi car designed to meet European Stage II standards. After 1,000 road miles, the embodiment was tested according to the European Stage III test protocol. The following test results were obtained:

	HC (g/Km)	CO (g/Km)	NO _x (g/Km)	PM (g/Km)
Engine-out exhaust gas	0.21	0.69	0.65	0.10
With Fig 4 by-pass filter	0.02	0.03	0.62	0.02

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It is to be noted that these results meet Stage IV requirements also, with the exception of NO_x. However, established engine design/management techniques can be used to lower NO_x emissions to Stage IV levels, with a consequent increase in Particulate Matter, but the system of the invention is capable of dealing with such emissions.

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It will be appreciated that there are many possibilities to vary the designs shown herein without departing from the principles of the present invention.

CLAIMS

1. An emission control system for exhaust gases from diesel engines, especially light duty diesel engines, comprising a source of NO_2 and a particulate trap, characterised in that
5 at most 85wt% of engine-out particulates are collected on the trap and combusted in the presence of said NO_2 in said trap.
2. A system according to claim 1, wherein the source of NO_2 is a catalyst which is effective to convert at least a portion of the NO in the exhaust gases to NO_2
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3. A system according to claim 2, wherein the exhaust gases pass through the catalyst before passing through the trap.
4. A system according to claim 1, 2 or 3 wherein an exhaust gas by-pass is provided
15 so that a portion of the exhaust gas does not pass through the filter.
5. A system according to claim 4, wherein said by-pass is effective only when substantial trapping of unburnt particulates has occurred.
- 20 6. A system according to claim 4 wherein said by-pass is effective under all operating conditions and at least 50wt% of particulate matter is trapped and combusted.
7. A system according to any one of the preceding claims, arranged such that at least 50wt% of particulate matter is trapped and subsequently combusted when operating
25 conditions in the same or subsequent operating cycle are improved.
8. A system according to any one of the preceding claims, in combination with NOx control means.
- 30 9. A system according to claim 8, wherein the NOx control means comprises a NOx absorbent.

10. A system according to claim 9, wherein said NO_x absorbent is effective to trap NO_x at relatively low exhaust gas temperatures, and releases NO_x when the exhaust gas temperature exceeds about 250°C for conversion and/or consumption in the combustion of particulate matter.

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11. A method of controlling emissions, especially particulate matter, from diesel engine exhaust gases by trapping and subsequently combusting said particulate matter, comprising trapping at most 85wt% of particulate matter in said exhaust gas and combusting said trapped particulate matter in the presence of NO₂.

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12. A method according to claim 11, comprising using an exhaust gas by-pass such that at least 50wt% of particulate matter is collected and combusted, and the exhaust gas by-pass is effective only when there is complete or substantial blocking of the trap.

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Fig.1.

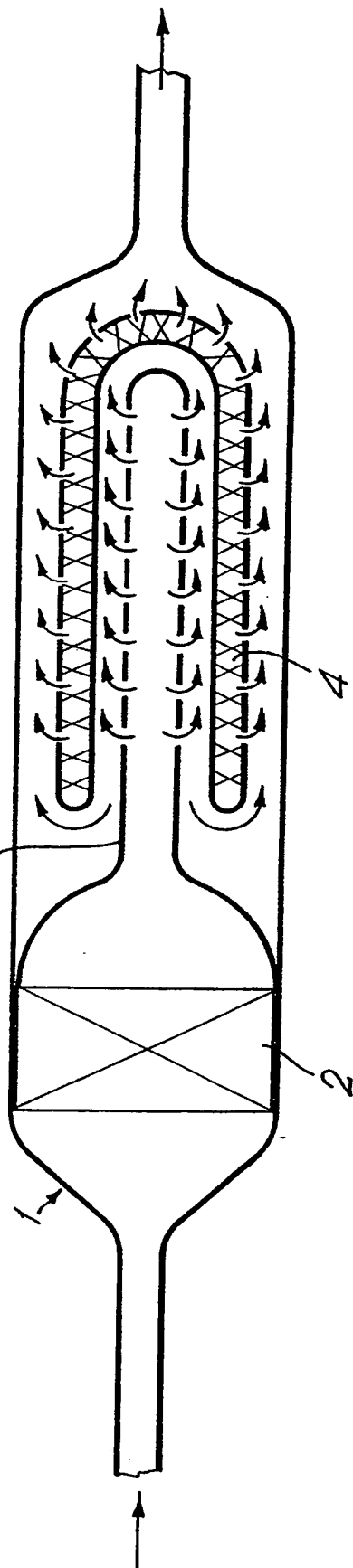


Fig.2.

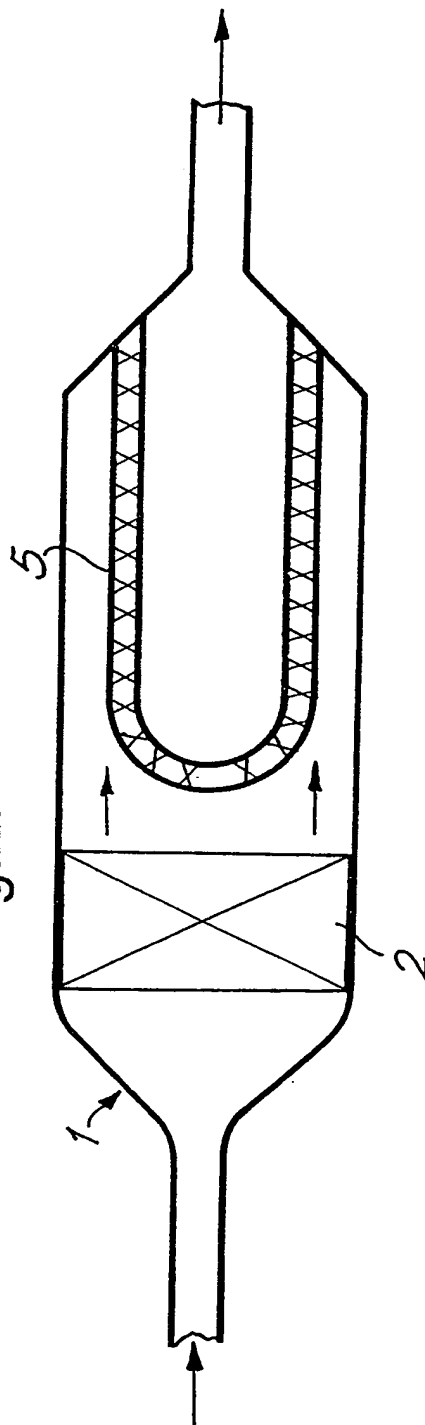


Fig.3.

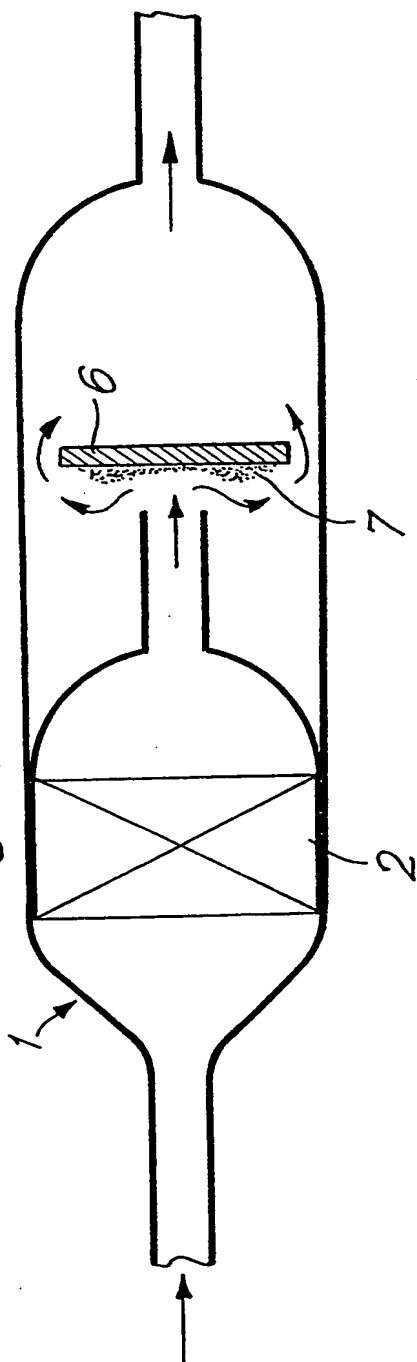
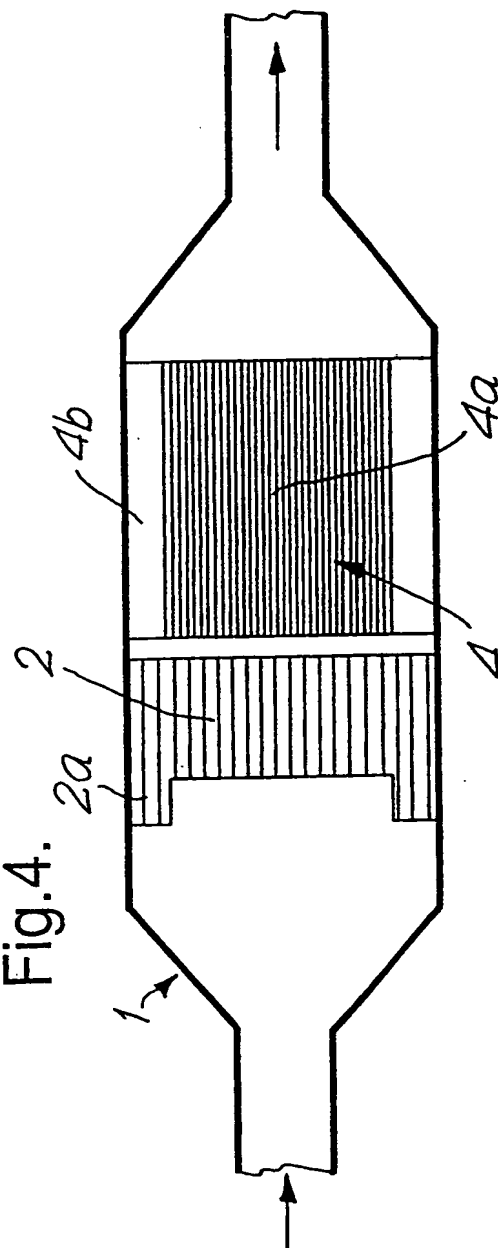


Fig.4.



INTERNATIONAL SEARCH REPORT

Intern: 11 Application No
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A. CLASSIFICATION OF SUBJECT MATTER
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According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 B01D F01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 758 713 A (TOYOTA MOTOR CO LTD) 19 February 1997 see column 2, line 41 - column 3, line 22	1-3,8-10
X	EP 0 341 832 A (JOHNSON MATTHEY INC) 15 November 1989 cited in the application see page 2, line 43 - line 51	1-3,11
A	DE 33 37 903 A (REIF GERHARD;BAUM WERNER) 9 May 1985 see figure 1	1,2,11

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

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Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0758713	A	19-02-1997	JP 9053442 A	25-02-1997
			US 5746989 A	05-05-1998
EP 0341832	A	15-11-1989	US 4902487 A	20-02-1990
			AT 132940 T	15-01-1996
			DE 68925382 D	22-02-1996
			DE 68925382 T	15-05-1996
			DK 233389 A	14-11-1989
			ES 2081301 T	01-03-1996
			GR 3018800 T	30-04-1996
			IE 71167 B	29-01-1997
			JP 1318715 A	25-12-1989
DE 3337903	A	09-05-1985	NONE	

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